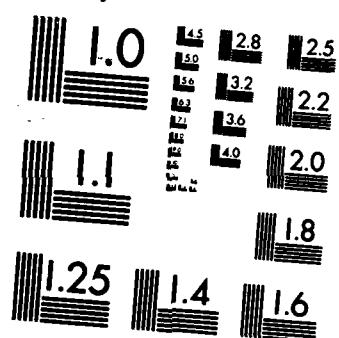


AD-A173 455 SILYLATED PHOSPHINES AND PHOSPHORANIMINES(U) TEXAS 1/1  
CHRISTIAN UNIV FORT WORTH DEPT OF CHEMISTRY  
R H NEILSON ET AL. 10 OCT 86 TCU/DC/TR-86-02  
UNCLASSIFIED N00014-79-C-0632 F/G 7/3 NL





MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

UNCLASSIFIED  
SECURITY CLASS

AD-A173 455

## DOCUMENTATION PAGE

(12)

1a. REPORT SET <u>Unclassified</u>		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) Texas Christian University Fort Worth, Texas 76129		7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy St. Arlington, VA 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER NO0014-79-C-0632	
8c. ADDRESS (City, State, and ZIP Code) see block 7b		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Silylated Phosphines and Phosphoranimines			
12. PERSONAL AUTHOR(S) R.H. Neilson, et al.			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) 10/10/86	15. PAGE COUNT 4
16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Navy position, policy, or decision, unless so designated by other documentation.			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) aminophosphine      silylaminophosphine phosphoranimine      → methylenephosphine.	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p><b>DTIC FILE COPY</b></p> <p>The N-silylphosphoranimines [e.g., <math>\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)\text{Me}_2</math>] undergo a variety of reactions including deprotonation/substitution of the P-Me groups, transylation, and condensation with reactive phosphines. Some new 1,2-addition and oxidation reactions of the P=C systems, <math>\text{R}_2^{\text{H}}\text{NP}=\text{CHR}</math>, <math>\text{R}_2^{\text{H}}\text{NP}(-\text{NR})=\text{CHR}</math>, and <math>\text{R}_2^{\text{H}}\text{NP}=\text{CR}-\text{CH}=\text{CHR}</math> (<math>\text{R} = \text{SiMe}_3</math>) are also reported. <i>Key words:</i> —</p> <p><b>DTIC ELECTED</b> OCT 23 1986</p> <p>76 10 21 05</p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH

Contract NOOO14-79-C-0632

R&T Code 413a001---01  
Replaces Old  
Task # 056-123

Technical Report No. TCU/DC/TR-86-02

Silylated Phosphines and Phosphoranimines

by

R.H. Neilson, B.A. Boyd, D.A. DuBois, R. Hani,  
G.M. Scheide, J.T. Shore, and U.G. Wettermark

Prepared for Publication

in

Phosphorus and Sulfur

Texas Christian University  
Department of Chemistry  
Fort Worth, Texas 76129

October 10, 1986

Accession For	
NTIS	GRA&I
DTIC TAB	<input checked="" type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/ _____	
Availability Codes	
Dist	Avail and/or Special
A-1	

Reproduction in whole or in part is permitted for  
any purpose of the United States Government.

\* This document has been approved for public release  
and sale; its distribution is unlimited.



## SILYLATED PHOSPHINES AND PHOSPHORANIMINES

ROBERT H. NEILSON\*, BRUCE A. BOYD, DONN A. DUBOIS,  
RAHIM HANI, GARY M. SCHEIDE, JOHN T. SHORE, AND  
URSZULA G. WETTERMARK

Department of Chemistry, Texas Christian  
University, Fort Worth, Texas 76129, USA

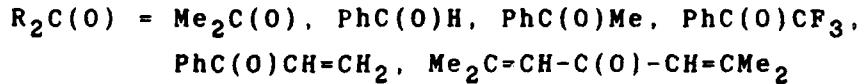
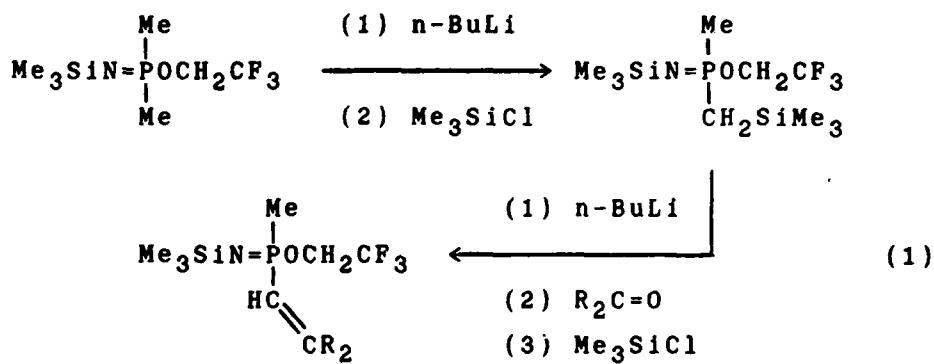
**Abstract** The N-silylphosphoranimines [e.g.,  $\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)\text{Me}_2$ ] undergo a variety of reactions including deprotonation/substitution of the P-Me groups, transilylation, and condensation with reactive phosphines. Some new 1,2-addition and oxidation reactions of the P=C systems,  $\text{R}_2\text{NP=CHR}$ ,  $\text{R}_2\text{NP(=NR)=CHR}$ , and  $\text{R}_2\text{NP=CR-CH=CHR}$  ( $\text{R} = \text{SiMe}_3$ ) are also reported.

The chemistry of compounds containing Si-N-P and/or Si-C-P linkages is usually markedly different from that of the nonsilylated analogues. On the one hand, the Si-N or Si-C bonds may function as reactive sites so that processes such as transilylation and condensation reactions via silane elimination are commonly found. Alternatively, the steric and electronic properties of the silyl groups can impart both kinetic stability and interesting chemical reactivity to a variety of low-coordinate phosphorus systems. We report here several illustrative examples of these principles.

### REACTIONS OF N-SILYLPHOSPHORANIMINES

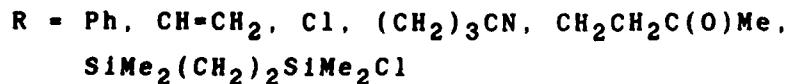
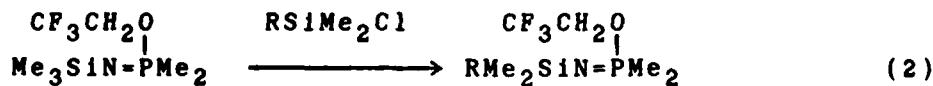
Various P-functionalized N-silylphosphoranimines are useful precursors to cyclic and polymeric phosphazenes. Recently, the synthetic utility of such compounds has

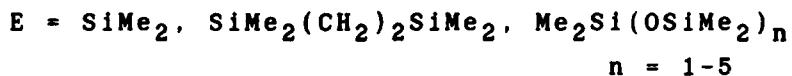
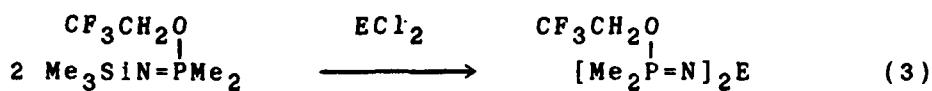
been greatly expanded through two general types of reactions. First, deprotonation/silylation of the P-methyl group followed by a Peterson olefination affords a series of vinyl derivatives (eq 1). Some of these



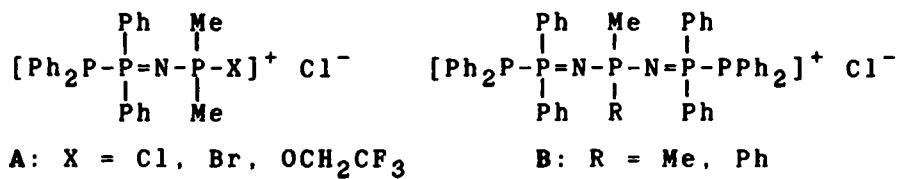
"monomers" undergo condensation polymerization to yield poly(phosphazenes) bearing substituted C=C side groups.

Second, we have studied a broad spectrum of Si-N bond cleavage reactions. For example, transilylation processes yield a series of novel N-silylphosphoranimines (eq 2) bearing reactive substituents on silicon as well as some bis(phosphoranimino)silanes and -siloxanes (eq 3). The related reactions involving cleavage of the Si-N bond in  $\text{Me}_3\text{SiN=P(X)Me}_2$  [X = Cl, Br,  $\text{OCH}_2\text{CF}_3$ , and  $\text{N(SiMe}_3)_2$ ] by reactive phosphines, e.g.,  $\text{Ph}_2\text{PY}$  (Y = Cl,  $\text{OCH}_2\text{CF}_3$ ), are generally more complex.





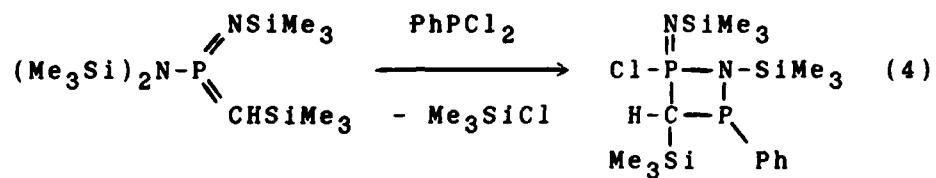
These reactions occur with elimination of  $\text{Me}_3\text{SiY}$  and, depending upon the choice of reactants, lead to various open-chain ionic species (e.g., A and B).



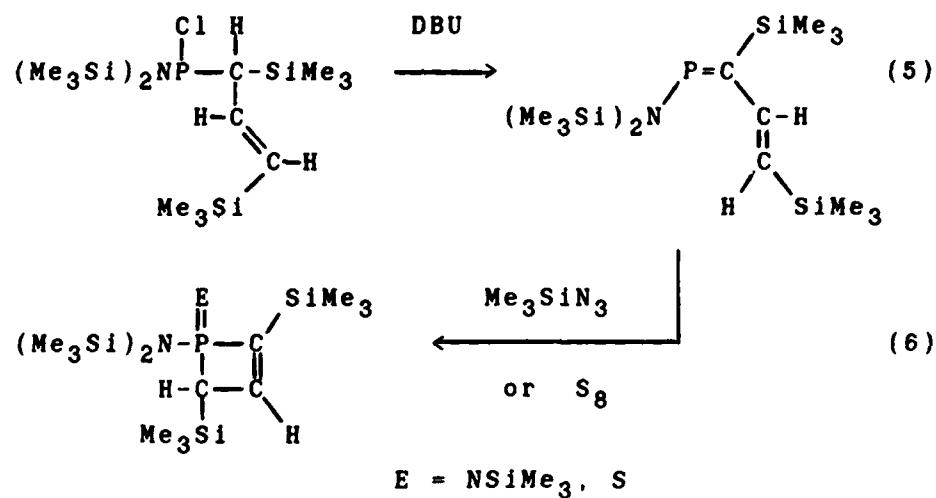
Surprisingly, the permethylated analogue of A ( $\text{X} = \text{OCH}_2\text{CF}_3$ ) is produced in high yield in the "transilylation" of  $\text{Me}_2\text{SiHCl}$  with  $\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)\text{Me}_2$ .

#### REACTIONS OF SILYLATED P=C COMPOUNDS

In this area our recent work has included a comparative study of the reactivity of the P=C bonds in the analogous P(III) and P(V) compounds,  $(\text{Me}_3\text{Si})_2\text{NP}=\text{CHSiMe}_3$  and  $(\text{Me}_3\text{Si})_2\text{NP}(-\text{NSiMe}_3)=\text{CHSiMe}_3$ , respectively. In general, the 1,2-addition of polar reagents to the P=C bond occurs more readily in the P(V) system. For example, while the former does not react with  $\text{PhPCl}_2$ , the latter undergoes Si-N cleavage and ring formation (eq 4) subsequent to the 1,2-addition process. Some reagents, on the other hand, react smoothly with both substrates. Cyclopentadiene, for example, affords a Diels-Alder adduct in each case.

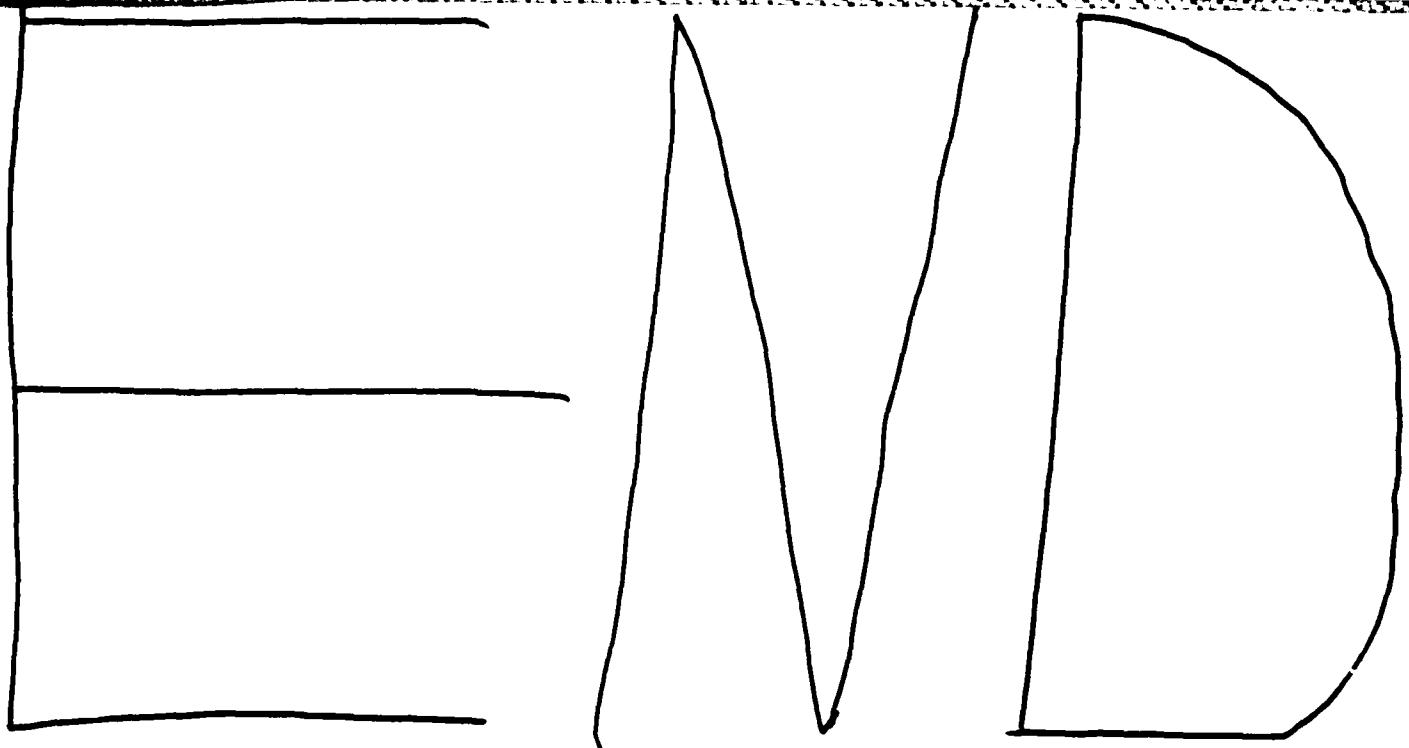


A stable, acyclic 1-phosphadiene has also been prepared (eq 5) and we have begun to investigate its derivative chemistry. Interestingly, simple oxidation reactions (e.g., with sulfur or  $\text{Me}_3\text{SiN}_3$ ) are accompanied by isomerization to four-membered ring products (eq 6). In the sulfur reaction, a three-membered disulfide ring,  $(\text{Me}_3\text{Si})_2\text{NP(S)-S-C(SiMe}_3)\text{CH=CHSiMe}_3$  is also produced.



#### ACKNOWLEDGEMENTS

This research is generously supported by the U.S. Army Research Office, the U.S. Office of Naval Research, and the Robert A. Welch Foundation.



12 - 86

